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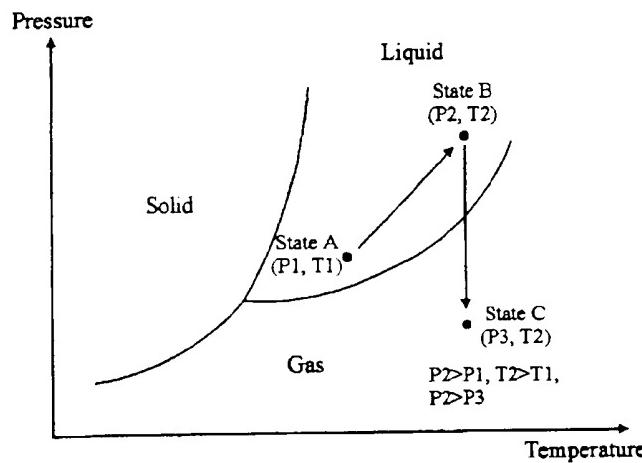
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(54) Title: METHOD OF VAPORIZING LIQUID SOURCES AND APPARATUS THEREFOR



WO 01/36702 A1

(57) Abstract: A method and apparatus for vaporizing liquid source materials, where such vaporized source materials are supplied to a deposition tool such as Chemical Vapor Deposition (CVD) apparatus, and more particularly in such areas as Metalorganic Chemical Vapor Deposition (MOCVD) and Atomic Layer Deposition (ALD) applications. The method disclosed herein

is a method for maintaining the liquid source material in a vessel and for dispensing the liquid source material in a instantaneous manner, and for maintaining the liquid source material in the vessel at a constant temperature, and for reducing the low pressure makes the liquid source material vaporized so that such vaporized source material can be supplied to such deposition tools as Metalorganic Chemical Vapor Deposition (MOCVD) and Atomic Layer Deposition (ALD) apparatus. The structure and the operation of the apparatus that vaporizes liquid source materials in accordance with the present invention are also disclosed.

## METHOD OF VAPORIZING LIQUID SOURCES AND APPARATUS THEREFOR

### TECHNICAL FIELD

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The present invention relates to a method of vaporizing liquid source materials for supplying such vaporized source materials to Chemical Vapor Deposition(CVD) apparatus, and more particularly in such 10 areas as Metalorganic Chemical Vapor Deposition(MOCVD) and Atomic Layer Deposition(ALD) applications.

### BACKGROUND ART

15 As a part of semiconductor device manufacturing processes, it has been active in developing methods of Chemical Vapor Deposition (CVD) processes, more particularly, in such areas of Metalorganic Chemical Vapor Deposition (MOCVD) and Atomic Layer Deposition (ALD) 20 applications, in order to form high quality films by using metalorganic source materials. However, since most of the metalorganic source materials are in either liquid state or solid state at room temperature, it is necessary to vaporize such source materials before they are supplied to 25 the reaction chamber of the Chemical Vapor Deposition(CVD) apparatus.

As a result, several different methods of vaporizing liquid or solid source materials have been proposed, among which the simple one is to heat the source material to 30 certain temperature until the source material evaporates.

However, this method is neither suitable for the materials which are thermally unstable at the vapor temperature, nor suitable for the materials of which the

liquid source material made of a solid source material by dissolving it with a solvent, the solvent vaporizes before the solute does. This means that the liquid becomes viscous easily or generate solute particles as it gets exposed in the atmosphere for a period of time. Therefore, it is difficult to maintain a steady flow of the source materials since the vapor pressure of the source material changes in time due to, for example, either high viscosity compared to the fresh liquid source material or the change of the surface area of solute particles. As a result, steady supply of vaporized source material at a constant rate becomes difficult.

Other methods of vaporizing the source materials either in liquid state or solid state have been suggested by R. H. Thring [U.S. Patent 5,836,289(1998)]. In order to increase the speed of evaporation, Thring (Porous Element Fuel Vaporizer) proposed to use a heated porous element to push liquid source material through it, and at the same time, carrier gas is also pushed through the porous element so that the mixture of the vaporized source material and the carrier gas is supplied to the desired reactor.

Li, et al [U.S. Patent 5,835,677(1998)] suggested to use an ultrasonic injection nozzle in conjunction with the method suggested by Thring aforementioned in order to improve the efficiency of the vaporization before the vaporized source material is forced into a CVD reaction chamber.

Another improved invention is suggested by J. H. Ewing [U.S. Patent 5,553,188(1996)] by using a stack of coaxially aligned, thermally conductive, thin, flat disks having different diameters, thereby allowing to form liquid films over a large surface area of the disks so that when carrier gas is forced into this large area coated with a film formed by the liquid source material, the carrier gas

the large surface area on the disks.

However, all the previous methods described above using either porous elements or a stack of coaxially aligned, thin, flat disks have a common problem of getting 5 clogged with the source material deteriorated in time due to easy condensation or solidification of the liquid source material in the small and narrow areas, thereby a smooth flow of the source material into the reaction chamber of a CVD is disturbed by such clogging.

10

#### DISCLOSURE OF THE INVENTION

The object of the present invention is to resolve the problems with the prior arts described above, that is, to 15 steadily and in desired quantities supply the necessary source materials to the reaction chamber of a CVD by vaporizing liquid source materials whether they are in liquid form originally or, in case of a solid source material, dissolved one by using appropriate solvent in 20 order to make it in liquid form.

Another object of the present invention is to supply the necessary source materials in a fashion of periodic pulsation to the reaction chamber of a CVD.

Another object of the present invention is to 25 disclose an apparatus for vaporizing liquid source materials at a steady rate, whereby the flow of the vaporized liquid source material can be easily controlled, and also the clogging in the vaporizer can be eliminated.

Another object of the present invention is to 30 disclose an apparatus for vaporizing liquid source materials in a fashion of periodic pulsation.

Yet another object of the present invention is to disclose an apparatus for vaporizing liquid source materials where the deteriorated source material in the

reservoir without dumping the deteriorated source material into the reaction chamber of a CVD apparatus.

For Chemical Vapor Deposition(CVD) process applications, it is desirable to supply vaporized liquid 5 source materials to the reaction chamber of a CVD apparatus. This invention discloses a method and apparatus for vaporizing liquid source materials for CVD applications, more particularly, in such areas as, but not limited to, Metalorganic Chemical Vapor Deposition(MOCVD) and Atomic 10 Layer Deposition(ALD) applications.

According to the present invention, a liquid source material at an equilibrium state at temperature T1 and pressure P1 is heated and pressurized to another equilibrium state at higher temperature T2 and higher 15 pressure level P2 in such a way that the liquid source material is not vaporized during this process. In accordance with the present invention, the liquid source material is pushed through a small opening instantaneously to a lower pressure state, such as P3 where P3 is lower than P2, while the temperature T2 is maintained at a similar level, in order to vaporize the liquid source material, during which period the liquid source material becomes vaporized due to sudden drop in pressure as well as due to sudden exposure to a low pressure state.

25 This invention also discloses apparatus for vaporizing liquid source materials using the method described above. The apparatus comprises a relatively small vent tube capped with a membrane-like flat surface, a reservoir for the liquid source material, a discharge tube 30 for the vaporized source material, a heating element that heats the liquid source material to keep the temperature of the liquid source material at an appropriate temperature, and finally a pressure pump that supplies the desired

The present invention has an advantage of requiring only a small exposed area or the area around said vent tube with a flat cap for vaporizing the liquid source material, reducing the possibility of being clogged up due to the 5 fact that the excessive liquid source material is turning into a viscous state around the capping area.

Several variations of vaporization apparatus are also disclosed.

All objects, features, and advantages of the present 10 invention will become apparent in the following detailed written description after a brief description of the drawings.

#### BRIEF DESCRIPTIONS OF THE DRAWINGS

15

The present invention itself, as well as preferred modes and advantages thereof, will best be understood by reference to the following detailed description of illustrative embodiments when read in conjunction with the 20 accompanying drawings, wherein:

Fig. 1 is a state diagram for a given source material showing the boundaries of the gas, liquid and solid states as a function of temperature and pressure;

Fig. 2A is a cross-sectional view of an exemplary 25 design of an apparatus in accordance with the present invention;

Fig. 2B is another cross-sectional view of Fig. 2A viewed along the line A-A' in Fig. 2A;

Fig. 3 is a cross-sectional view of another exemplary 30 design of the apparatus with a vertical carrier gas tube as well as a mechanically pressurized stopper design in accordance with the present invention;

Fig. 4 is a cross-sectional view of another exemplary design of apparatus with a vertical carrier gas tube and a

present invention;

Fig. 5 is a cross-sectional view of an improved design of the apparatus shown in Fig. 4;

Fig. 6 is a cross-sectional view of an exemplary 5 design of an apparatus with a hybrid type of carrier gas tube, which is a combination of a horizontal inlet carrier gas tube and a vertical outlet carrier gas tube in accordance with the present invention;

Fig. 7 is a cross-sectional view of an improved 10 design of the apparatus shown in Fig. 6 for faster flow of the carrier gas so that the vaporized source material can be carried out to the reaction chamber faster in accordance with the present invention;

Fig. 8A is a cross-sectional view of an apparatus 15 with more efficient pick-up means of the vaporized source material by the carrier gas in accordance with the present invention; and

Fig. 8B is a cross-sectional view of the apparatus in Fig. 8A viewed along the line B-B' in accordance with the 20 present invention.

#### MODES OF CARRYING OUT THE INVENTION

In accordance with the present invention, referring 25 to Fig. 1, given a liquid source material of which the state is initially in an equilibrium state(state A) at the temperature T1 and the pressure P1, the source material is heated and pressurized until it reaches a new equilibrium state(state B) at higher levels of temperature T2 and 30 pressure P2 in such a way that the liquid source is not vaporized during the transition. In Fig. 1, this process is illustrated by an arrow going from the state A to the state B.

state, for example, P3 while the temperature of the liquid source material is maintained at the same level of T2(state C). During this transition, the liquid source material is pushed into an open space in a collecting tube or a vent 5 with a low level of pressure P3 while the temperature of the liquid source material is kept at the same level of T2. In Fig. 1, this process is illustrated by an arrow going from the state B to the state C.

During the transition going from the high 10 temperature-high pressure state B to the high temperature-low pressure state C in Fig. 1, the liquid source material is vaporized since the state of the source material is instantaneously changed from the liquid state B to the gas state C under the same temperature T2. The vaporized 15 source material produced by this method is collected appropriately and fed into the reaction chamber of a CVD.

In accordance with another aspect of the present invention, an apparatus that vaporizes the liquid source material and collects the resultant vapor source material 20 as well as supplies it steadily into the reaction chamber of a CVD, comprises a liquid source material supply line, a reservoir that contains the liquid source material fed through said supply line, a vent with a stopper that opens and closes by means of mechanical or fluidic pressure and 25 also allows the pressurized liquid source material to pass through the stopper to get exposed instantaneously into a low pressure state so that the liquid source material is vaporized during the sudden transition from a high pressure state to a low pressure state, and a gas transport tube 30 that carries the vaporized source material to a desired destination such as the reaction chamber of a CVD.

According to the present invention, said apparatus also contains a pressure pump that supplies the liquid source material to the reservoir under certain desired

to the stopper, by either mechanical or fluidic means, so that the vent is in a closed position when the pressure of the liquid source material is less than the stopper pressure pressed by a pressurizer, and the vent opens when 5 the pressure of the liquid source material is higher than the stopper pressure. Normally, the stopper pressure is kept at a fixed level, as an example, slightly higher than P2 when the apparatus is not in use.

Finally, said apparatus is also optionally equipped 10 with a heater that heats the liquid source material to a level of temperature T2, if it needs to be, depending upon the type of the liquid source material used. Certain source materials need to be heated, and others do not.

The present invention will best be understood by 15 reference to the following detailed exemplary and preferred embodiments.

The present invention may be realized in a variety of ways in implementing the method of vaporizing the desired liquid source materials aforementioned.

Some of the sample source materials in liquid state 20 at atmospheric condition are TEOS [tetraethoxyorthosilicate, Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>], Tantalum pentaethoxide [Ta(OCH<sub>2</sub>CH<sub>3</sub>)<sub>5</sub>], Titanium isopropoxide [Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>], Zirconium tert-butoxide [Zr[OC(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>], Hafnium tert-butoxide 25 [Hf[OC(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>], TDMAT [tetrakisdimethylamidotitanium, Ti[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>], TDEAT [tetrakisdiethylamidotitanium, Ti[N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>], (hfac)Cu(vtms), where hfac means hexafluoroacetylacetone and vtms means vinyltrimethylsilane, and some of the typical source 30 materials in solid state requiring solvents such as toluene, THF(tetrahydrofuran) and n-butyl acetate to change into liquid state are Ba(thd)<sub>2</sub>, where thd means tetramethylheptanedionate, Sr(thd)<sub>2</sub>, Bi(thd)<sub>3</sub>, La(thd)<sub>3</sub>, Pr(thd)<sub>3</sub>, Cr(thd)<sub>3</sub>, Cu[Te(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, and Cu(hfac)<sub>2</sub>.

configurations of the apparatus for vaporizing liquid source materials for supplying to the reaction chamber of a CVD in accordance with the present invention are disclosed and presented herein. Those who are knowledgeable in the art should be able to easily perform other designs, structures and configurations as desired within the spirit of the present invention. Therefore, the scope of the designs, structures and configurations in accordance with the present invention is not limited to the preferred embodiments presented here.

Preferred Embodiment 1

Referring now to the Fig. 1, which is a phase diagram showing the boundaries between solid, liquid and gas states for a give liquid source material as a function of temperature and pressure, a liquid copper source material in the equilibrium state of atmospheric pressure(1 Atm.) and room temperature is pressurized to 12.3 Atm., that is,  $P_2=12.3$  Atm., while the temperature stayed virtually about the same, that is,  $T_1 \approx T_2 \approx$  room temperature. The stopper pressure is set at about 12.3 Atm. When the pressure of the liquid source material is increased and reached at 12.3 Atm. and eventually exceeds the threshold pressure of 12.3 Atm. for the stopper, the liquid source material passed through the vent, and got instantaneously exposed to the pressure, as an example, for the MOCVD processes, which is typically several Torr or less, thereby the liquid source, which was at the pressure level of 12.3 Atm., became vaporized due to sudden drop in pressure from 12.3 Atm. to a low pressure, and was discharged through the ventilation tube, which is a part of the vent.

Preferred Embodiment 2

Show in Fig. 2A is a cross-sectional view of an exemplary apparatus in accordance with the present 5 invention. Fig. 2B is another cross-sectional view of Fig. 2A viewed along the line A-A' in Fig. 2A.

The exemplary apparatus of the vaporizing apparatus comprises main body 110 and the optional heater 120. The main body 110 comprises supply tube 112, reservoir 114, 10 vent 116, vent tube 142, gas discharge tube 118, stopper 140, pressurized contact surface 124, inlet carrier gas tube 126, outlet gas tube 128, pressurized 130 and, pressure tight contact 132. The height of the vent tube 142 provides the desired space for the reservoir 114. The 15 pressure pump 150(not shown) is connected to the supply tube 112.

The optional heater 120 that heats the main body as well as the liquid source material in the reservoir 114 is shown in both Fig. 2A and Fig. 2B.

Referring to Fig. 2A and Fig. 2B a liquid source 20 material is supplied by the pressure pump 150(not shown) through the supply tube 112 until the reservoir 114 is filled with the liquid source material, which is under pressure at a level of, for example,  $P_1$ . The liquid source 25 material in the reservoir 114 remains within itself because the pressurizer 130 pushes the stopper 140 downward so that the stopper makes a tight surface contact with the vent. This provides pressurized contact surface 124. The stopper 140 also tightly inside the main body 110, thereby both the 30 main body and the stopper make a good pressure tight contact 132. Therefore, as long as the pressurizer 130 pushes the stopper 140 downward against the vent 116 at a higher level than the pressure state of the liquid scurce material itself in the reservoir 114, the liquid source

The pressure of the stopper 140 pressing down against the vent 116 is now set at P2, and the pressure inside the reservoir 114 is increased by using the pressure pump 150(not shown) and, at the same time, the temperature of 5 the liquid source material in the reservoir 114 is increased to T2 by using the heater 120. When the temperature of the liquid source material is raised to T2 and the pressure inside the reservoir 114 is increased to 10 pass P2 by using the pressure pump 150(not shown), then, as soon as the pressure inside the reservoir 114 exceeds P2, the liquid source material pushes the stopper upward and this action opens the vent 116. Since this occurs almost 15 instantaneously, the liquid source material passes through the vent around the top surface of the ring of the vent 114 and is exposed instantaneously to a low pressure state of the inside of the vent, thereby the liquid source material is vaporized and is discharged through the vent tube 142, and eventually it is pushed through the gas discharge tube 118, where a carrier gas flows through the gas discharge 20 tube 118 and picks up the vaporized source material. The mixture of the vaporized source material and the carrier gas passes though the outlet gas tube 128 and then to the reaction chamber of a CVD.

There are several modes of operation in terms of the 25 vent opening. The first mode is to maintain the pressure of the liquid source material high enough so that the stopper 140 is kept in the lifted-up position and, as a result, the vent 116 is in the open position, thereby the liquid source material flows through the vent steadily and 30 continuously, and therefore, the vaporized source material is steadily and continuously supplied through the outlet gas tube 128. The second mode is to maintain the pressure difference between the stopper 140 and the liquid source material at an appropriate level so that the vent 116

source material is supplied in a fashion of periodic pulsation.

In either mode of operations, the amount of the flow of the vaporized source material can be controlled by a  
5 metering pump of which the outlet pressure can exceed the pressure of the stopper. Those two modes aforementioned can be controlled by adjusting the outlet pressure of the metering pump.

For the periodic pulsation mode, the abruptness of  
10 the stoppage of the supply of the source material is dependent upon the performance of the metering pump.

Preferred Embodiment 3

15 An exemplary design of an apparatus for vaporizing liquid source material with a mechanical pressurizer is disclosed and presented here.

Referring to Fig. 3, the proposed apparatus is another aspect of the apparatus disclosed and presented in  
20 the Preferred Embodiment 2 above with the exception of vertical carrier gas tube 226 and 228, vertical supply tube 212 and, more significantly, a mechanical stopper 240 and a clear-out tube 213, which is closed during a normal operation.

25 As the pressure in the reservcir 214 is increased until it exceeds the threshold pressure of the stopper 240, which have a spring effect upward, the liquid source material in the reservoir 214 pushes the stopper 240 and the pressurized contact surface 224 at the top surface of  
30 the vent 216 opens, and the liquid source material in the reservoir 214 passes through the vent opening, which is the top part of the vent 216. Then, due to a sudden exposure into a low pressure state in the vent 216 as well as the gas discharge tube 218 area, the liquid source material

Subsequently, the carrier gas in the gas discharge tube 218 picks up the vaporized source material and travels through the outlet gas tube 228, and then, eventually to the reaction chamber of a CVD.

5 Other operational functions and workings not described here are the same as the ones described in the Preferred Embodiment 2 above. As an example, the flow of the vaporized source material can be controlled by adjusting the pressure in the metering pump. The use of  
10 the heater 220 is optional depending upon the nature of the liquid source material used. The clean-out hole 213 is for cleaning the reservoir after a lengthy use of the apparatus.

This is one example of many possible designs with mechanically pressurized stopper, where the pressurizer may 15 potentially be eliminated. However, a pressurizer, either mechanical or fluidic may be added when one is needed additionally.

#### Preferred Embodiment 4

20 Shown in Fig.4 is another aspect of an apparatus that vaporizes a liquid source material in accordance with the present invention.

The subject apparatus shown in Fig.4 has a ring-like 25 stopper 340 with the vertically mounted inlet carrier gas tube 326 and the outlet carrier gas tube 328. The subject apparatus has a mechanical pressurizer 330. The main body 310 has a clean-out hole for cleaning the reservoir 314.

The functions and workings of the apparatus disclosed 30 and presented here, are similar to the apparatus disclosed and presented in the preferred embodiment 2.

As shown in Fig.5, an improved design of the apparatus in Fig.4, is also disclosed and presented. The outlet gas tube 42° with larger diameter than the inlet gas

material coming from the gas discharge tube 416 and the carrier gas to flow more smoothly through the gas discharge tube 418 compared to the apparatus shown in Fig. 4.

5 Preferred Embodiment 5

Another apparatus for vaporizing liquid source material in accordance with the present invention as shown in Fig. 6 is disclosed and presented here. This apparatus 10 has a "horizontal" inlet gas tube 526 and a "vertical" outlet gas tube 528. Due to the close proximity of the vent tube 542, the gas discharge tube 518 and the stopper 540, this structure provides a better mixing and discharging ability of the vaporized source material and 15 the carrier gas.

An improved apparatus in Fig. 6 presented above is also disclosed and presented here as shown in Fig. 7. This is an improvement over the apparatus in Fig. 6 in terms of yet better mixing capability of the vaporized source 20 material and the carrier gas due to the shape of the stack that is connected to the inlet gas tube 626 as well as the vent tube 642. This shape provides better gas turbulence near the stopper so that the vaporized source material and the carrier gas are mixed faster and uniformly.

25 The basic functions and workings of the apparatuses disclosed and presented here, are similar to the apparatus disclosed and presented in the Preferred Embodiment 2.

Preferred Embodiment 6

30

Yet another exemplary apparatus for vaporizing liquid source material as shown in Fig. 8A with a cross-sectional view as shown in Fig 8B along the line B-B' in Fig. 8A is disclosed and presented here.

shape of structure made of the vent tube 742 and the gas discharge tube 718 as shown in Figs. 8A and 8B. The gas mixing wall 717 provides a better gas mixing function without an elaborate design. The height and width of the  
5 gas mixing wall 717 can be adjusted for proper rate of mix of the source and carrier gases as well as the flow of carrier gas through the inlet gas tube 726 and the outlet gas tube 728. The mechanical partitioning of the mechanical parts can be made in many different ways in such  
10 a way that their machining, assembly, disassembly, cleaning and other maintenance become convenient and easy.

In the preferred embodiments described above, some of the exemplary designs, structures and configurations of the apparatus for vaporizing liquid source materials for  
15 supplying to the reaction chamber of a CVD in accordance with the present invention are disclosed and presented herein. Those who are knowledgeable in the art should be able to easily perform other designs, structures, configurations, and variation as derived within the spirit  
20 of the present invention. Therefore, the scope of the designs, structures, configurations in accordance with the present invention is not limited to the preferred embodiments presented here.

What is claimed is:

1. A vaporizing method comprising the steps of:  
5 changing the equilibrium state of a liquid at temperature T<sub>1</sub> and pressure P<sub>1</sub> to a new equilibrium state with a higher temperature T<sub>2</sub> and a higher level of pressure P<sub>2</sub> without vaporizing the liquid source material; and  
10 exposing the liquid source material instantaneously into a lower level of pressure state P<sub>3</sub> in order to vaporize the liquid source material, where T<sub>2</sub>≥ T<sub>1</sub> and P<sub>2</sub>>P<sub>1</sub> ≥ P<sub>3</sub>.
2. An apparatus that vaporizes a liquid source material, collects the resultant vapor source material by means of carrier gas and supplies the resulting gas to a desired destination, the apparatus comprising:  
15 a liquid source material supply line that supplies pressurized liquid source material;  
20 a reservoir that contains pressurized liquid source material;  
25 a vent with a stopper that opens and closes instantaneously by the pressure change in the reservoir so that the sudden exposure to a low pressure state causes vaporization of the liquid source material when the vent opens instantaneously;  
30 a vent tube that allows the vaporized source material to be transported out or vented out;  
a gas transport tube that carries the vaporized source material by means of carrier gas to a desired destination;  
35 a pressurizing means that keeps the liquid source material within the reservoir by means of a stopper; and  
a heating means that heats the liquid source material to a desired level of temperature when needed.

3. The apparatus of claim 2, in which the top part of reservoir is left open, and the stopper completes the closure of the reservoir, the stopper moves up and down, the stopper makes a tight surface contact with the top part of the vent, and the vent tube provides a space for the reservoir by limiting the stopper coming down further even though the pressurizing means pushes the stopper downward.
- 5
4. The apparatus of claim 2, in which a metering pump is connected to the liquid source supply line and the pressure level is adjusted in such a way that the flow of the liquid source material through the vent is constant, thereby a constant and steady supply of the vaporized source material is attained and maintained.
- 10
- 15
5. The apparatus of claim 4, in which the pressure difference between the reservoir and the stopper is maintained at an appropriate level by adjusting the pressure of the metering pump so that the vent and the stopper repeat the open-and-close actions, thereby the vaporized source material is supplied in a fashion of periodic pulsation for easy control of the flow of the vaporized source material.
- 20
- 25
6. The apparatus of claim 2, in which the liquid source supply line, a clean-out line and gas transportation tube are connected vertically to the reservoir, and the pressurizing means is eliminated so that the stopper acts as a pressurizing means.
- 30
7. The apparatus of claim 6, of which the liquid source supply line is connected horizontally to the bottom part of the reservoir, a clean-out line is also connected, a stopper ring is inserted between the bottom of the inlet

8. The apparatus of claim 7, the bottom part of the outlet gas tube is enlarged so that the transport gas with the vaporized source material flows easily.

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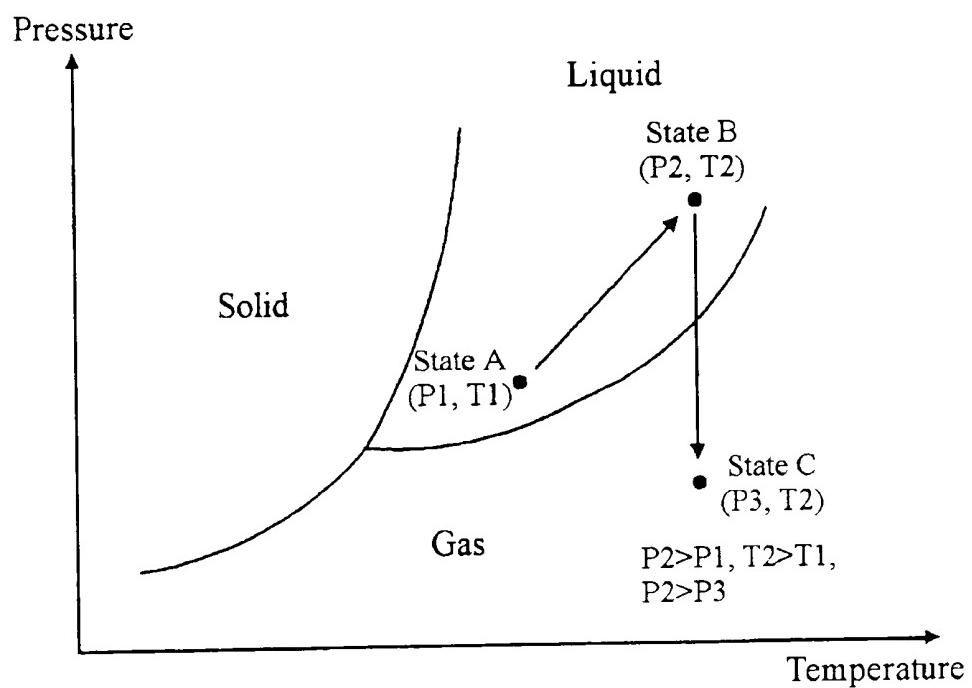
9. The apparatus of claim 2, of which the outlet gas tube is connected vertically inside the vent tube for better mix of gases, a clean-out line is added.

10 10. The apparatus of claim 9, of which the bottom part of the vent tube is enlarged for better mix and flow of the gases and a clean-out line is added.

11. The apparatus of claim 3, wherein a gas mixing wall  
15 with appropriate height and width is attached in the middle of the vent tube and the carrier gas transport tube, thereby providing a better mix of the gases.

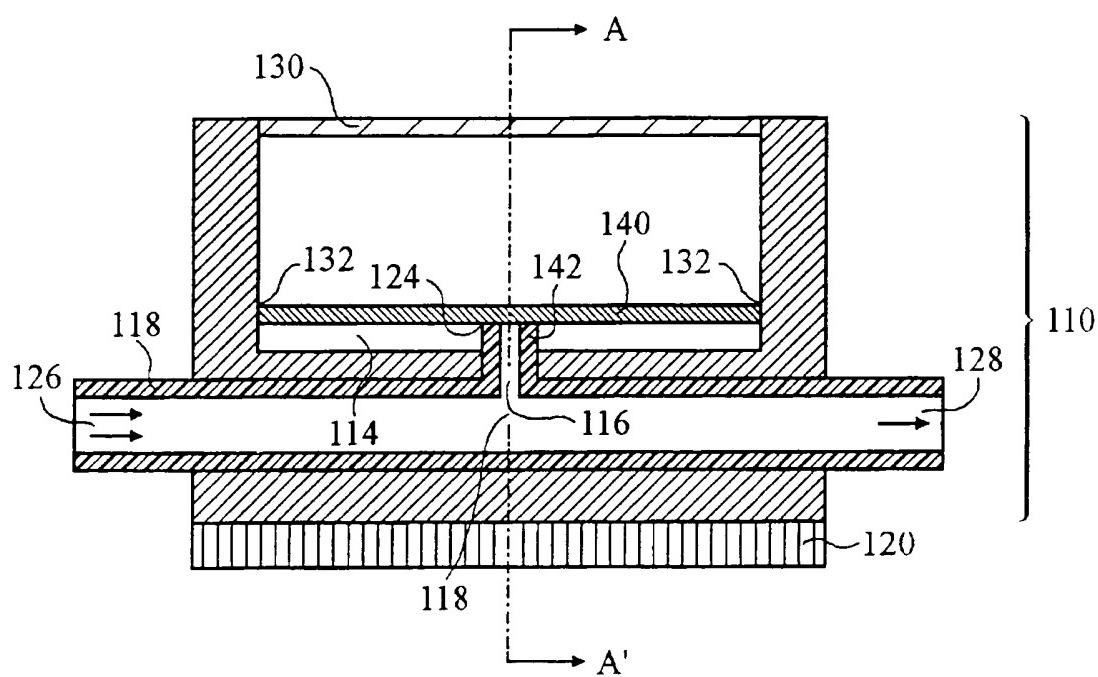
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Fig. 1

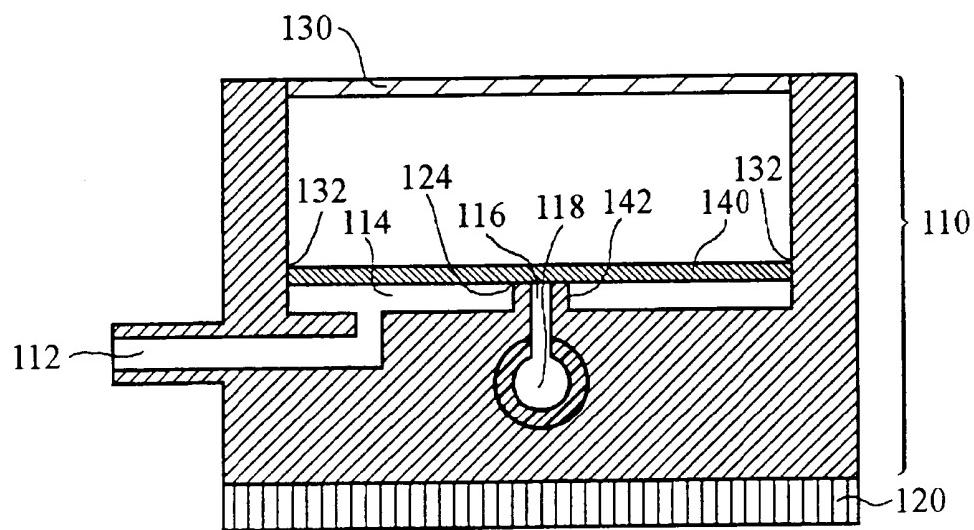


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Fig. 2A



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**Fig. 2B**

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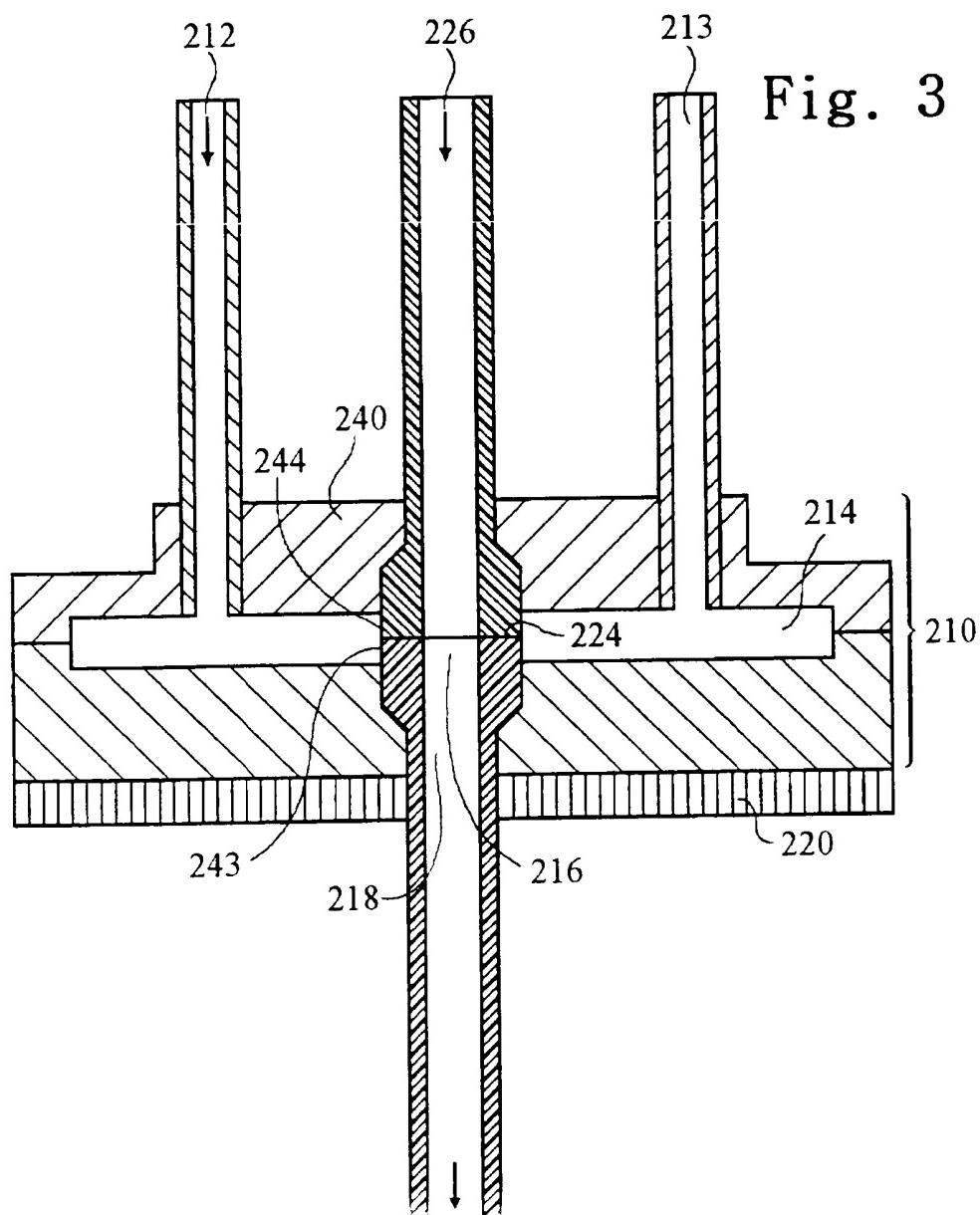
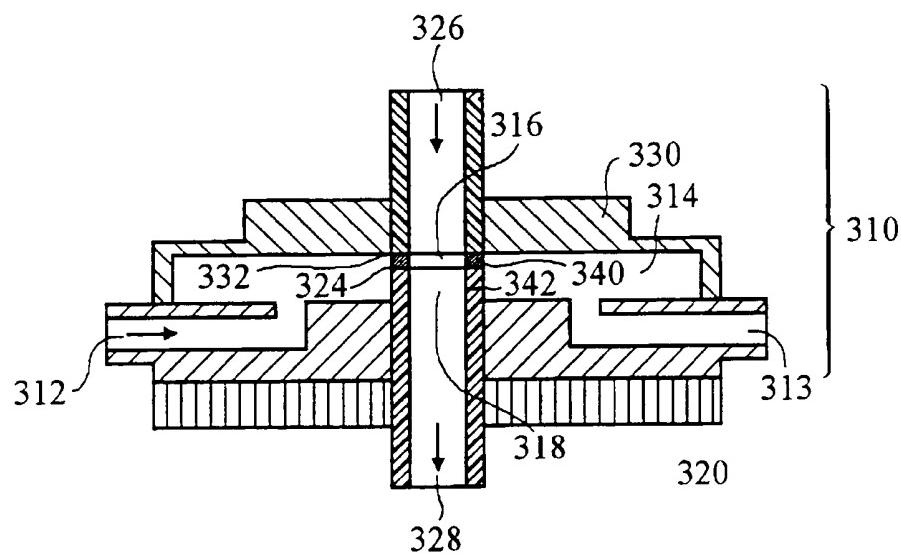


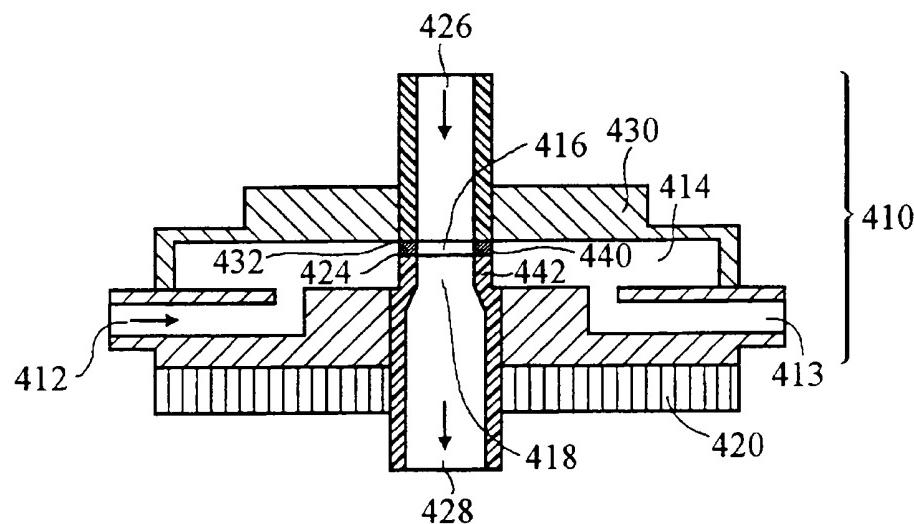
Fig. 3

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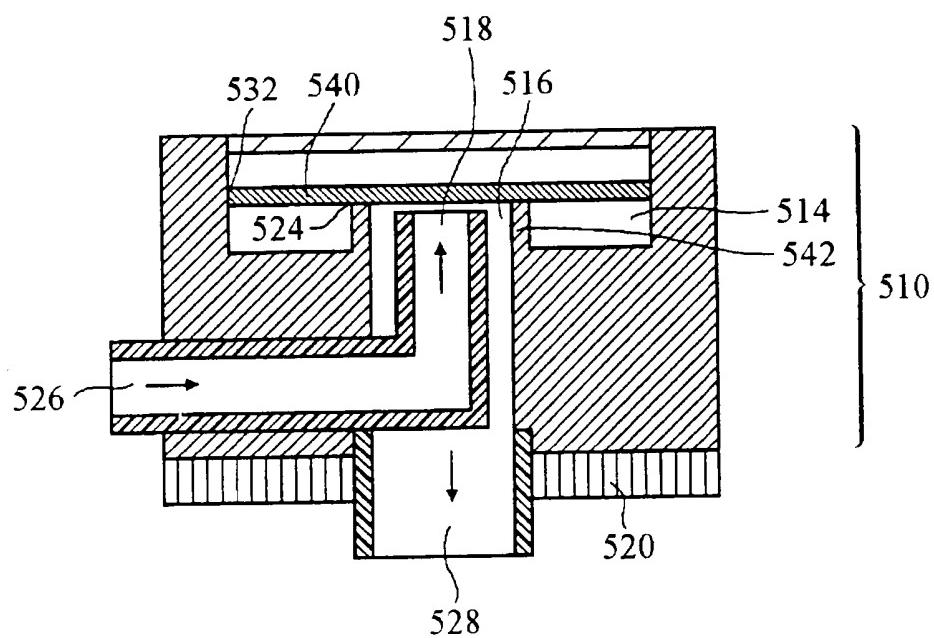
**Fig. 4**

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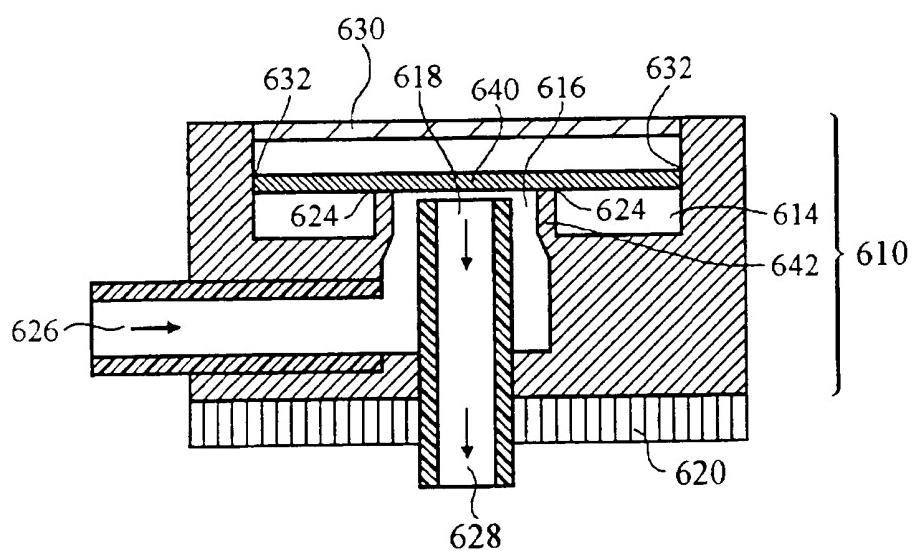
Fig. 5



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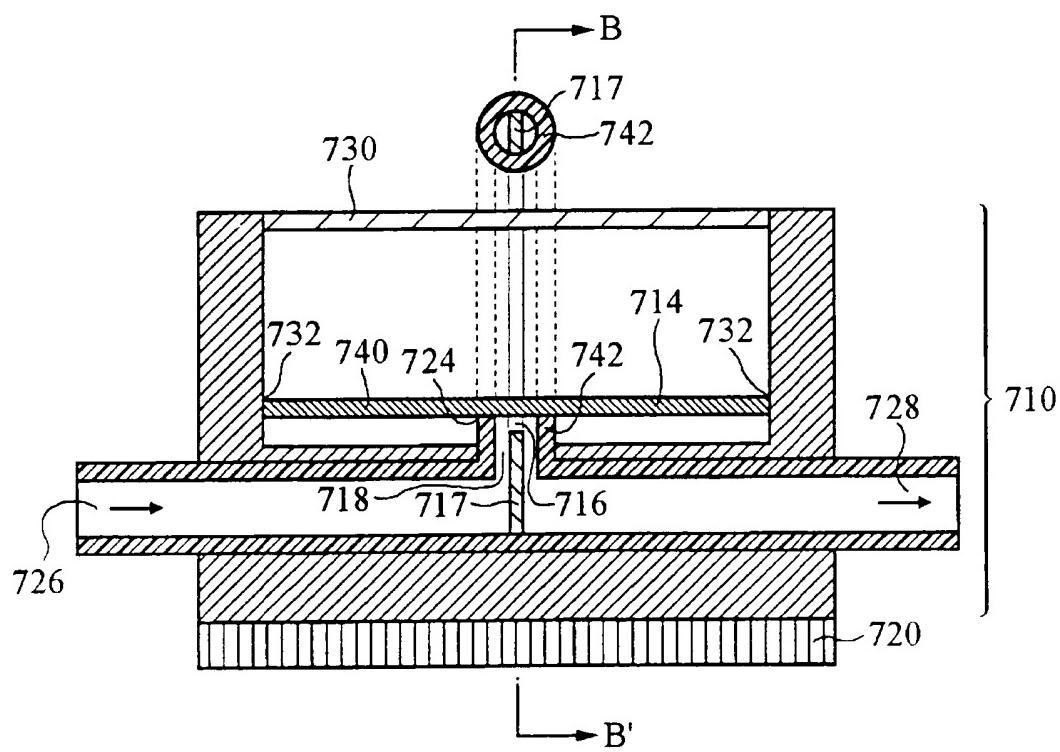
**Fig. 6**

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**Fig. 7**

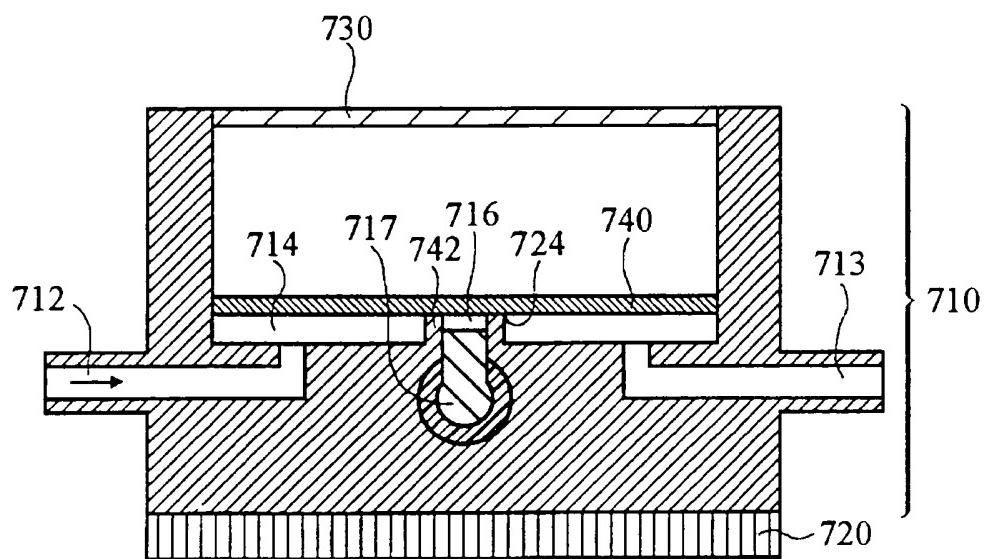
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Fig. 8A



10/10

Fig. 8B



## INTERNATIONAL SEARCH REPORT

International application No. PCT/KR 00/01331
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## CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: C23C 16/00, 22/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: C23C, C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel QPI and EPODOC; STN PATDPA; ELSEVIER; Delphion Int. Prop. Network

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GERTHSEN, KNESER, VOGEL. PHYSIK. Springer-Verlag Heidelberg Berlin New York, 1977, pages 187-191.  especially picture 534.	1
X	The Clausius-Clapeyron equation. [online] http://chem 132.stanford.edu/fall 99/chem 171/ Handouts/node 75.html. [retrieved on 13 February 2001 (13.02.01)] Retrieved from Internet Database.	1
A	US 5090985 A (SOUBEYRAND et al.) 25 February 1992 (25.02.92) claims, abstract. -----	2

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
• Special categories of cited documents:	..A" document defining the general state of the art which is not considered to be of particular relevance ..E" earlier application or patent but published on or after the international filing date ..L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) ..O" document referring to an oral disclosure, use, exhibition or other means ..P" document published prior to the international filing date but later than the priority date claimed	..T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention ..X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone ..Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art ..&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

15.02.2001 15.02.2001

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P. M. 1000/2001

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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/KR 00/01331

The cited documents show the state of art for vaporising liquids and preparing vaporised reactants for CVD means:

- 1) The **Textbook of physics** shows the equilibrium state of a liquid and ist vapor and the connection between temperature and pressure. The Clausius Clapeyron equation shows the connection.
- 2) The **internet page** shows the Clausius-Clapeyron equation and the connection of vapor pressure of gases and liquids.
- 3) US **5090985 A** describes the preparation of reactants for CVD by initially heating a liquid coating precursor, injecting the liquid coating precursor into a vaporization chamber, simultaneously admitting a blend gas into the vaporization chamber, heating the liquid and blend gas to cause the liquid to vaporize at a temperature below ist standard vaporization temperature, and thoroughly mixing the coating precursor vapor and blend gas, to produce a stream of vaporized reactants for pyrolytic decomposition.